Feb. 18, 1936. H. JOHN ET AL 2,031,485

METHOD OF BLEACHING PULP

Filed May 20, 1931 2 Sheets-Sheet 1

Fig. 1

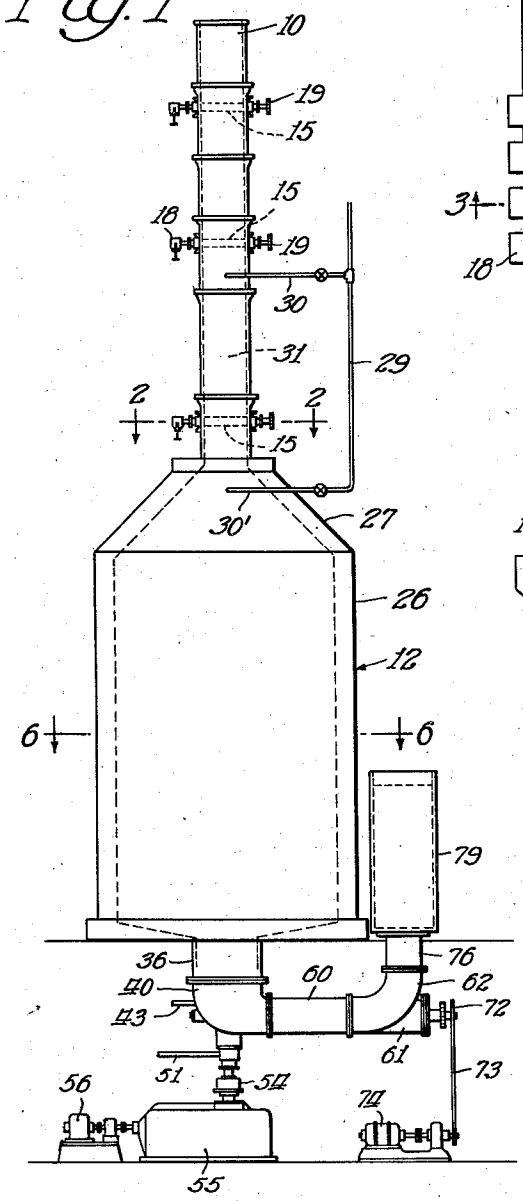


Fig. 2

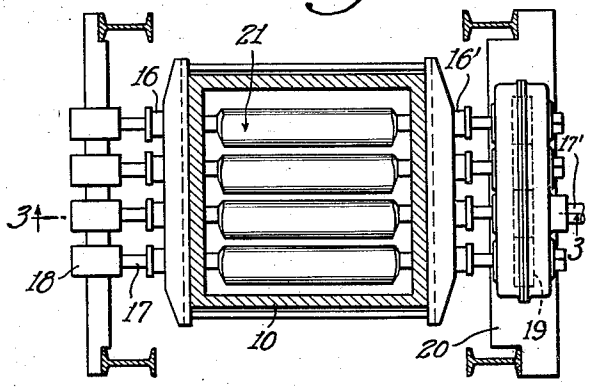


Fig. 3

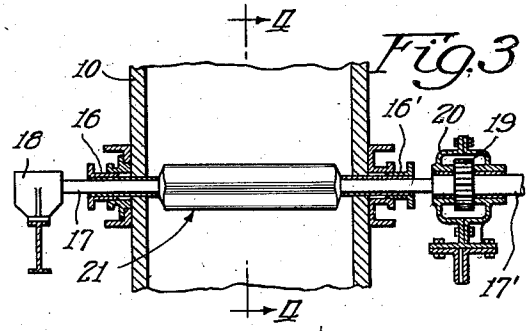
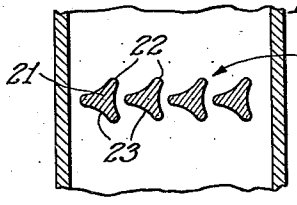


Fig. 4



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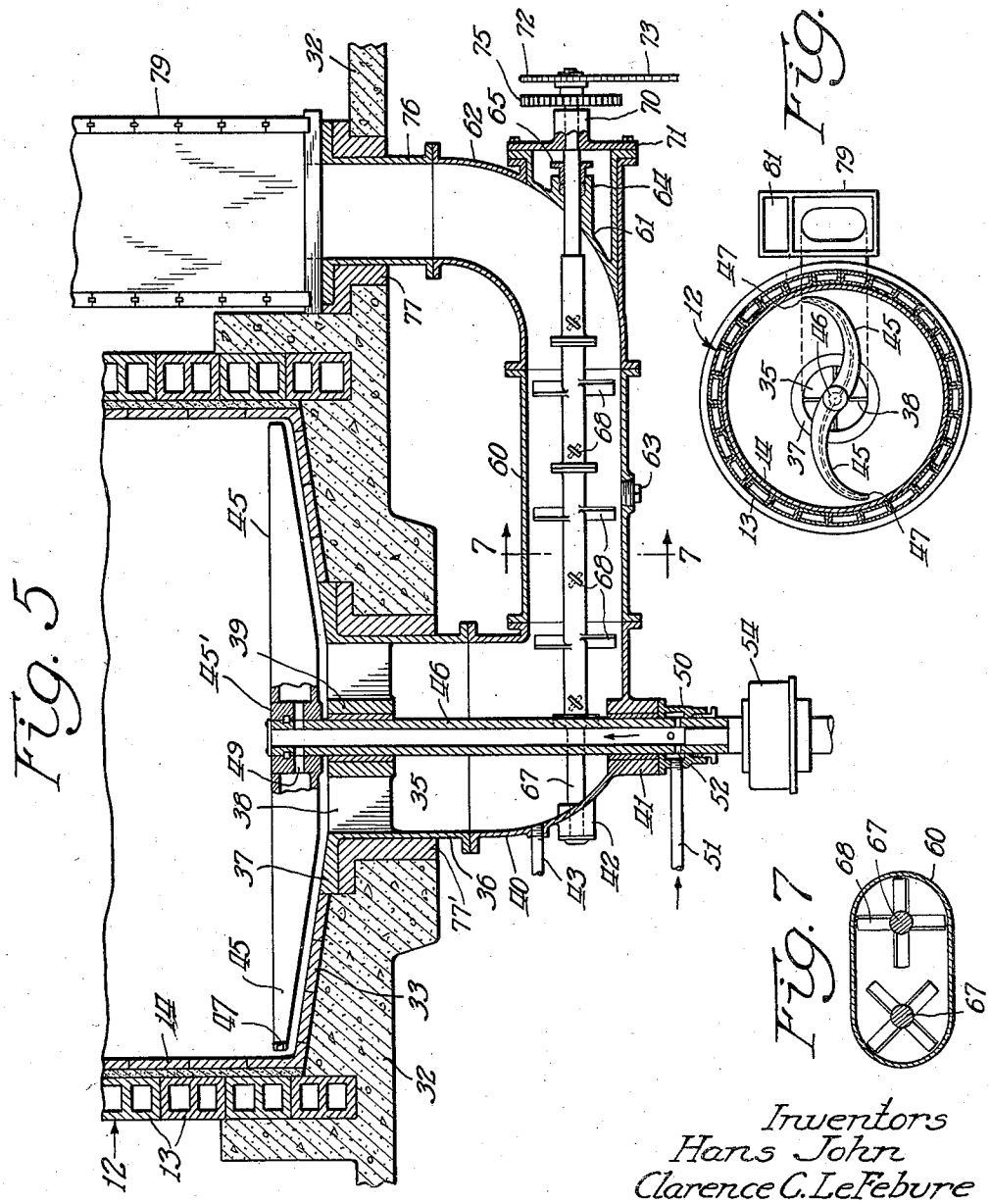


Fig. 5

Fig. 6

Fig. 7

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METHOD OF BLEACHING PULP

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Application May 20, 1931, Serial No. 538,650

30 Claims. (Cl. 8—2)

Our invention relates broadly to the bleaching of fibrous pulp such as is to be used in the manufacture of paper or similar products, and has particular applicability in connection with the treatment of sulphite pulp, although it will be readily understood that our invention may be used in connection with various other types of pulp and other materials.

Our invention contemplates effecting the bleaching of the pulp in a plurality of stages and has for its object the provision of a process which will be simple, expeditious, economical, and highly efficient, and which will result in the production of a pulp of exceptionally high quality. This process may be considered an improvement over that described in patent to Hans John, No. 1,872,743, granted August 23, 1932.

Another object is to provide new and improved apparatus for bleaching fibrous material which is especially adapted for use in connection with our improved process.

Various other objects and advantages will be come readily apparent as the description proceeds.

Referring now to the drawings forming part of this specification and illustrating a preferred embodiment of the improved apparatus:—

Fig. 1 shows an elevation of a bleaching tank and tower.

Fig. 2 is an enlarged sectional view taken substantially on the line 2—2 of Figure 1.

Fig. 3 is a sectional view taken on the line 3—3 of Figure 2.

Fig. 4 is a sectional view taken on the line 4—4 of Figure 3.

Fig. 5 is a fragmentary vertical sectional view, on an enlarged scale, of the lower portion of the tank and parts co-operating therewith.

Fig. 6 is a sectional view taken substantially on the line 6—6 of Figure 1, and

Fig. 7 is a sectional view taken on the line 7—7 of Figure 5.

In carying out our process, we start with unbleached chemical pulp suspended in water. While, as stated above, the process has particular applicability to sulphite pulp, it is not necessarily restricted thereto. The pulp is thickened to a consistency above 22 per cent (where consistencies are mentioned in this specification, it will be understood to be on a bone-dry basis), preferably about 25 per cent, although consistencies running considerably higher may be used. At the same time the pulp is formed into a continuous porous web. This may be accomplished on an Oliver filter or other suitable apparatus. The web is then shredded into relatively small pieces, preferably not over an inch in any dimension, and these pieces are then conveyed to the apparatus, shown in the drawings as by means of a belt conveyor or the like.

Turning now to the drawings, the improved apparatus comprises a tower 10 which is mounted over a tank 12. The tower 10 is preferably square in cross-section and may be formed of ceramic tile and may conveniently be built up in sections as clearly shown in Figure 1. Arranged at various points along the tower 10 is a plurality of feed grates 15. Referring more particularly to Figures 2 to 4, inclusive, each of these grates comprises a plurality of aligned stuffing boxes 16—16' extending on opposite sides of the tower and journaling parallel shafts 17. These shafts are retained by means of suitable thrust bearings (not shown) disposed in a housing 18 and carrying intermeshing spur gears 19, arranged in a housing 20. One of the shafts 17 of each grate projects, as at 17', for connection to a source of power (not shown) with a variable speed device, whereby each grate may be rotated at any desired speed independently of the others for regulating the feed of pulp that may be disposed thereon.

Each of the shafts 17 has fixed thereon within the tower, a feed-control member 21 forming part of the grate 15. These members, as best seen in Figure 4, are peculiarly formed whereby the pulp may be fed therebetween, while at the same time jamming of the grates, due to packing of pulp between the feed members, is avoided. It will be seen that each member 21 is in cross-section roughly in the shape of an equi-lateral triangle with the vertices rounded to form convex edges 22 and with the sides curved to form concave faces 23. The shafts 17 are, of course, rotated in opposite directions by means of their respective gears and the feed members 21 are arranged in identically the same position relative to the tower 10, as clearly shown in Figure 4, so that an edge 22 of each member will arrive in a horizontal plane simultaneously and thus will be disposed opposite a concave face 23 of an adjacent feed member.

The tank 12 with which the tower 10 communicates may be built of hollow tile 13 and lined with suitable acid-resisting ceramic material 14, and comprises a substantially cylindrical portion 26 and a frusto-conical dome portion 27 which supports and communicates with the tower 10. The numeral 29 represents a conduit for bleaching gas, such as chlorine or the like from which gas

is conducted through pipes **30** and **30'**, the flow of gas in these pipes being controlled by means of suitable valves. The pipe **30** is led into the tower **10** slightly below the second set of grates from the bottom, while the conduit **30'** admits gas into the upper portion of the dome **27**. A pile **31** of pulp is maintained on the grates.

Turning now to Figure 5, it will be seen that the tank **12** is supported in suitable masonry **32** which may be part of a floor, which masonry may be reinforced by suitable structural metal elements (not shown). The tank is provided with a slightly concave circular floor **33**, preferably formed of tile similar to the side walls **14** and leading to a central well **35**. (Figure 6.) This well is provided by means of a tubular member **36** flanged at its upper end, as indicated at **37**, which flange forms a portion of the floor of the tank. Adjacent the upper portion of the tubular member **36** is formed a spider **38** which supports a substantially vertical bearing **39**. The tubular member **36** communicates with an elbow **40** provided at its lower portion with a vertical bearing **41** aligned with the bearing **39** and on its side with a pair of substantially horizontal parallel bearings **42**, only one of which is seen in the drawings. A water pipe **43** communicates with the elbow **40**.

Arranged in the bottom of the tank is a hollow agitating member **45**. As best seen in Figures 5 and 6, this member has two blades or arms curved so as to be substantially S-shaped and thus provide a pair of pockets on the sides thereof in its direction of rotation. It will also be observed that the lower contour of this member conforms substantially to the concave formation of the bottom wall **33** of the tank. The agitator is provided with a collar **45'** whereby it is secured to a tubular shaft **46**. The hollow arms of the agitator **45** terminate in laterally extending nozzles **47** which point in the direction of rotation of the arms. As clearly shown in Figure 5, the hollow shaft **46** communicates with the agitator arms by means of suitable ducts in the shaft and in the collar **45'**, these ducts being represented generally by the numeral **49**. The shaft **46** is journaled in the bearings **39** and **41** and the lower portion thereof extends through a suitable stuffing box **50** with which communicates a water pipe **51**. The shaft is provided with ducts **52** whereby fluid may pass into the bore of the shaft. The shaft is connected through a suitable coupling **54** and reducing mechanism **55** to a motor **56** or other suitable source of power.

The elbow **40** is connected to a pipe section **60** which in turn is connected to an elbow **62**. The pipe section **60** may conveniently have a drain plug **63** at the bottom thereof. Projecting horizontally from the elbow **62** is a pair of stuffing boxes **61**, each having a packing ring **64** and gland **65**.

Journaled in each of the bearings **42** is a shaft **67** carrying a plurality of paddles or propeller blades **68** of any suitable design for moving the material through the pipe **60** and parts communicating therewith. The parallel shafts **67** are also journaled through the packing rings **64** and glands **65** and through bearings **70**. These bearings may each be formed integrally with a disk **71** which may be secured to the stuffing box as by means of bolts or the like. One of the shafts **67** has secured thereto outside of the bearing **70** a pulley **72** over which is trained a chain **73** connected to any suitable source of power, such as a motor **74**, or the like, whereby motion may be transmitted to the shaft **67** and to the propellers **68**. Motion is transmitted from one of the shafts **67** to the other through a gear **75**.

The elbow **62** is connected to a pipe section **76** which may be anchored in the concrete **32** and retained by means of grout **77** or the like. The section **36** may be similarly secured as by means of grout **77'**.

The pipe section **76** communicates with a wier box **79**, from which the flow may be controlled by means of an adjustable dam.

PROCEDURE

First stage

In the operation of the device just described in accordance with our process, the pulp which has been thickened and shredded as above described, is delivered to the top of the tower **10** and dumped therein. Its passage through the tower is controlled by means of the rotating feed grates **15**. These grates serve to control the flow of pulp into the tank **12**, which may be referred to as the reaction chamber, and are so operated as to maintain a pile of pulp on top of each one, which acts as a gas seal, the piles, however, being so adjusted that there will be space between each pile and the grate above it (see Figure 1).

It might be mentioned at this point that various other constructions may be provided for feeding material to the reaction chamber **12** which would also serve as a gas seal therefor, in lieu of the tower described and illustrated. Thus, I might feed the pulp into the chamber by shoving it by means of a suitable propeller through a tube, this tube being either horizontal or slightly inclined upwardly toward the point of discharge, which would be at or adjacent to the top of the reaction chamber. A screw conveyor, plunger, or other suitable means might be used to propel the stock in the tube, which would be moved in such a manner as always to have therein a mass of unbleached pulp through which any escaping gas would have to pass, whereby the gas would be effectively prevented from escaping.

The bleaching gas, preferably chlorine, is introduced at all events through the conduit **30'** whereby it is permitted to flow over the pulp lying in the tank. As shown, the gas may also be introduced through the conduit **30** above one or more of the feed grates. The falling of the shredded pulp through the gas affords intimate mixing therewith. The amount of gas introduced is proportioned to the degree of bleaching desired, generally between 50 and 80 per cent of complete bleaching. As our process is carried out, we preferably accomplish about **65** per cent bleaching at this stage.

The pulp is allowed to accumulate in the tank in a pile deep enough to reach economically practical exhaustion of the gas at the bottom of the pile. The arms **45** are continuously rotated during the conduct of the bleaching operation and water sprayed out of the nozzles **47**. It will be seen that water is thus only injected into the bottom layer of the pulp and affects that portion which is passing out of the tank through the well **35**. The height of the pulp in the tank is controlled by varying the amount of water injected into the bottom which, by controlling the fluidity of the pulp, varies the readiness with which it flows out of the tank. Milk of lime is preferably added to the water injected into the tank through the rotating arms to neutralize enough of the acid liberated during the gassing treatment so that the stock will not be too corrosive to the subsequent

equipment. At the same time the lime accelerates the exhaustion of any remaining traces of chlorine in the stock, thus preventing discomfort to the personnel and corrosion of equipment when the stock is removed from the tank.

The height of the water level in the bottom of the tank is controlled by the dam in the wier box. The level is preferably so adjusted as to have water above the scrapers **45**, thus protecting them from the corrosive action of the traces of chlorine and hydrochloric acid in the stock. The water also acts as a seal to the outlet.

The pile of stock in the bottom of the tank functions to enable the reaction between the chlorine and the pulp to go on at a rapid rate, due to the relatively higher concentration of the chlorine in the moisture of the high consistency stock, as compared with what that concentration would be if the stock were diluted immediately with water.

Another function of the pile of stock is to act practically as a seal to prevent access of the chlorine in the top of the tank to the water in the bottom and thus avoid dissolving too much chlorine in the water. The combined effect of these two functions is that the chlorine mixed with the pulp is practically exhausted before the stock is mixed with the water. If, on the other hand, much chlorine were mixed into the water at the outlet, either the time necessary for exhausting, if alkali were not added, would be excessively long, or the economy of chemicals would suffer from undesirable side reactions on dissolved substances in the water.

The tank is discharged through the well **35**, which, as stated above, serves as a water seal, the stock being moved from the sides toward the well **35** by means of the rotating arms **45**, water being projected ahead of the arms from the spouts **47**. Thus, the consistency of the pulp is lowered by admixture with water so that, due to the action of the rotating arms and the pressure of the pile of pulp, the mixture will flow out of the tank at the rate necessary to maintain the top of the pile at the desired height. The consistency of the pulp is further lowered by admixture with water from the pipe **43** to from 1.5 to 2 per cent, in which condition the mixture flows very much like water. The material passes down the well through the pipe section **36**, elbow **40**, pipe **60**, elbow **62**, and pipe **76** into the box **79**, the paddles **68** serving to propel and also to mix the material to a smooth consistency.

The material flows over the dam in the wier box **79** and thence flows through a down-spout **81** into a storage tank (not shown) below. By adjusting the level of the dam the water level in the reaction tank may be controlled as stated above.

From the storage tank, which is used mainly to eliminate the fluctuations in the discharge from the reaction tank, the stock is pumped to a thickener, which again may be an Oliver filter, where the stock is reduced again to a consistency of between 20 and 25 per cent. It is evident that the dilution of the stock after the gassing, followed by the thickening, constitutes a dilution washing. This may be increased by a displacement wash on the thickener, or by additional washing machines, if desired.

Pulp prepared as above described is not at all white and requires further bleaching for most purposes. Such bleaching may be effected, for example as described under Second Stage below.

Furthermore, while the following bleaching operation may advantageously follow the steps described above, nevertheless, it may be used with excellent results on pulp which has been prebleached by various other processes. Thus, for example, we may use pulp which has been prebleached according to the following procedure:—

Alternative first stage (pre-bleaching)

The pulp may be pre-bleached by mixing with it a sufficient quantity of so-called calcium hypochlorite bleach to give a high degree of prebleaching (as high as 80 per cent is good), and adding enough acid to make the mixture strongly acid. Two gallons or more of sulphuric acid per ton of pulp may be used. Low pH values are advantageous. The reaction should be carried on with little friction between the fibers; therefore, we prefer to operate at a consistency of 4 per cent or less and do not agitate violently after the initial thorough mixing. Temperature is not important except to control the time necessary for exhaustion. The more acid the mixture, the lower the temperature necessary to complete this stage in a given time. We prefer room temperature.

Also, the more acid the mixture, the more nearly the product corresponds to pulp prebleached to the same degree with chlorine gas. At the end of this pre-bleaching, the stock is washed and thickened in a similar manner to the procedure for gas-treated pulp.

Second stage

For our purpose the stock is removed from the thickener at the end of the first stage at a consistency between 20 and 25 per cent. This is limited by the mechanical characteristics of the thickener. It is then mixed with sufficient alkaline bleach liquor (calcium base bleach containing an excess of calcium hydroxide) to obtain a suspension of fiber having a low viscosity (we use consistencies of 4 per cent or less). The available chlorine content of the bleach liquor is adjusted to give a concentration of about 1 to 1.5 grams of available chlorine per liter of liquor at the end of the alkaline phase of the process. This is an excess of from one to twenty times the quantity of bleach consumed in this stage. The calcium hydroxide content of the bleach is maintained high enough to have an excess present until the excess of bleach has been removed and the concentration of available chlorine lowered as hereinafter set forth.

Room temperature may be used during this stage, but it is more expedient to use temperatures from 30 C. to 35 degrees C., in order to complete the bleaching in a suitable time and avoid too much tankage.

From the mixer the stock is pumped to tanks, where it is allowed to remain with little or no stirring until it is ready for the next stage. We particularly avoid violent agitation during this stage to prevent the damage to the fiber which results from friction between the fibers rubbing off the protective substances normally present in this method of bleaching.

The length of time that the pulp is subjected to the above treatment is determined by the color and cleanliness obtained at the end of the subsequent stage. Our experience has shown about three hours to be sufficient with hemlock sulphite pulp of ordinary bleachability and cleanliness.

When the reaction has progressed far enough

as above determined, the stock is pumped to a thickener, such as an Oliver filter, and most of the excess of bleach removed, the resulting consistency being regulated to suit the requirements of the next stage and the mechanical limitations of the thickener. We prefer to thicken to about 20 to 25 per cent.

In recovering the bleach liquor care is exercised not to dilute it, because it may be brought back to its original active chemical strength and reused in the second stage of the treatment of another batch of stock.

At the end of the alkaline stage the pulp is still somewhat yellow. It has not reached the desired bright color, but this is easily and quickly obtained by the subsequent treatment.

The important points in the above stage are:—

First.—The bath is alkaline, which is desirable after the pre-bleaching has rendered the fiber sensitive and which aids in protecting it from injury from the high concentration of bleach maintained to the end of the stage.

Second.—The concentration of bleach is maintained as high as is possible without damage to the pulp and excessive chemical loss in order to obtain a sufficiently rapid reaction for economy of time and to have as vigorous a reaction as possible upon the shives and dirt to the end of the stage.

The concentration of bleach in this stage does not undergo the relatively tremendous fall from initial to final concentration that occurs in ordinary bleaching practice, and, therefore, so far as this factor is concerned, any substances able to react with the bleach are subjected to approximately the same reaction rate throughout this stage.

Third.—Friction is avoided. This is of great importance because the stock is very easily damaged by friction in the presence of the high concentration of bleach.

Fourth.—The calcium ion concentration is high in the above procedure. This apparently exerts a strong protective action to the fiber against the destructive action of the bleach, possibly by rendering the reaction products insoluble in the liquor.

Third stage

The thickened stock is diluted with water to give a low consistency (about 4 per cent or less) and low bleach concentration (about 0.1 gram available chlorine per liter or less). Acid is added in quantity sufficient to render the mixture distinctly acid. (We preferably use about two gallons or more of sulphuric acid per ton of pulp). The stock is well mixed and allowed to react for a short time. About fifteen minutes usually is sufficient, although somewhat longer reaction time does not injure the pulp at these concentrations.

The remaining bleach is then destroyed by adding an antichlor such as sulphurous acid solution, and the pulp is well washed to remove the soluble impurities.

During this stage, the color changes to a bright white, but the pulp is not damaged as is usually the case in bleaching to a bright color.

By carrying out the bleaching in the second and third stages as above described, especially when they are preceded by pre-bleaching with elementary chlorine in the first stage to approximately two-thirds of the total bleachability, exceptionally white pulps are obtained having remarkably low alkali solubilities and copper numbers and high alpha-cellulose contents, without strength loss, with low shrinkage loss, and with low chemical consumption.

Advantages of our improved process

As compared with ordinary two-stage bleaching in which the usual bleach liquor is employed, or as compared with the chlorine water as commonly used in pre-bleaching, our use of gas in the first stage has the following advantages:

In the first place, we are able to effect an enormous reduction in the time required for the first stage.

In the second place, we are able to carry the actual bleaching to a point considerably in excess of 50 per cent of the total bleaching effect desired. In fact, with our process we find that it is highly desirable to carry it to a point beyond 50 per cent. On the other hand, with the well-known chlorine water treatment, which consists in merely subjecting pulp to the action of chlorine water without agitation it is necessary to prolong the treatment for many hours in order to complete the reaction. The time may be reduced by the use of heat, but this is expensive.

It has been found in previously known methods that damage to the pulp is due to the presence of relatively large amounts of bleach acting upon the exposed surface of the fibers under acid conditions for a relatively long time. All these factors must be present in order to result in any substantial damage to the fiber. Hence, if the other factors exist during the first stage while the fibers are still coated with their adherent protective material, no substantial damage results. However, in the latter part of the second stage the fibers have been denuded of their protective coating, and therefore it is essential that an alkaline condition exist.

One of the great advantages of our process resides in the fact that by employing a large excess of bleach which is only partially reduced by the end of the second stage, we are enabled, first, to insure the maintenance of an alkaline condition throughout the second stage; secondly, to reduce the time required for the second stage.

The continued alkalinity, however, is due to the fact that we employ a relatively low pulp density enabling us to hold in solution in the bath a sufficient amount of lime to maintain the alkalinity.

The reduction in the time required for the second stage is due also to the fact that, even at the end of the stage, there is enough bleach present to take care of the last remnants of foreign materials quickly, whereas in the ordinary bleaching process more refractory materials remaining at the end of the bleaching process are subjected to the action of relatively weak or spent bleach solution.

Another feature of our process resides in the fact that since we carry on the second and third stages, which are the most critical stages of the process, at a relatively low pulp density and without violent agitation, the fibers are not mechanically denuded of their protective coating and are therefore protected from deleterious chemical action.

Various changes, modifications, and improvements coming within the spirit of our invention will doubtless occur to those skilled in the art. Hence, we do not wish to be limited to the precise embodiments herein disclosed but wish to be limited solely by the scope of the appended claims, which are to be interpreted as broadly as the state of the art will permit.

We claim as our invention:

1. A process of bleaching cellulosic material and the like, comprising feeding said material in a porous, moist condition through a column of bleaching gas, feeding said material into a reaction chamber of relatively large cross-section as compared with said column, allowing said material to form a pile in said chamber and there react with a bleaching gas, introducing bleaching gas into the upper portion of said chamber, adding an aqueous diluent to the lower portion of said pile, and withdrawing said material from the lower diluted portion thereof.

2. A process of bleaching cellulosic material and the like, comprising feeding said material in a porous, moist condition downwardly through a column of bleaching gas, feeding said material into a reaction chamber of relatively large cross-section as compared with said column, allowing said material to form a pile in said chamber and there react with a bleaching gas, introducing bleaching gas into the upper portion of said chamber and into said column, adding an aqueous diluent to the lower portion of said pile, and withdrawing said material from the lower diluted portion thereof.

3. A process of bleaching cellulosic material and the like, comprising pre-bleaching said material, subjecting said material to a second stage of bleaching in a bath rendered alkaline with an alkali earth base and with the use of a relatively large excess of bleaching agent throughout the entire second stage, the conditions of the second stage being adjusted so as to preserve the fiber strength and avoid substantial dissolving action, and subjecting said material to a final bleaching stage under acid conditions for a relatively short period of time, said last two bleaching stages being conducted without any substantial amount of agitation.

4. A process of bleaching cellulosic material and the like, comprising pre-bleaching said material, subjecting said material to a second stage of bleaching in a bath rendered alkaline with an alkali earth base with the use of a relatively large excess of bleaching agent throughout the entire second stage, the conditions of the second stage being adjusted so as to preserve the fiber strength and avoid substantial dissolving action, and in the presence of calcium ions, and subjecting said material to a final bleaching stage under acid conditions for a relatively short period of time.

5. A process of bleaching cellulosic material and the like, comprising pre-bleaching said material, subjecting said material to a second stage of bleaching in a bath rendered alkaline with an alkali earth base, said second stage being conducted with a relatively low pulp concentration and a sufficiently high concentration of bleaching agent so that a substantial excess thereof remains at the completion of said second stage, the conditions of the second stage being adjusted so as to preserve the fiber strength and avoid substantial dissolving action, and in the presence of calcium ions, and subjecting said material to a final bleaching stage under acid conditions for a relatively short period of time.

6. A process of bleaching cellulosic material and the like, comprising pre-bleaching said material with a gaseous bleaching agent, subjecting said material to a second stage of bleaching in a bath rendered alkaline with an alkali earth base with the use of a relatively large excess of bleach throughout the entire second stage, the conditions of the second stage being adjusted so as to preserve the fiber strength and avoid substantial dissolving action, and subjecting said material to a final bleaching stage under acid conditions for a relatively short period of time, said last two bleaching stages being conducted with the absence of any substantial amount of agitation.

7. A process of bleaching cellulosic material and the like, comprising pre-bleaching said material with a gaseous bleaching agent, subjecting said material to a second stage of bleaching in a bath rendered alkaline with an alkali earth base with the use of a relatively large excess of bleach throughout the entire second stage, the conditions of the second stage being adjusted so as to preserve the fiber strength and avoid substantial dissolving action, and in the presence of calcium ions, and subjecting said material to a final bleaching stage under acid conditions for a relatively short period of time.

8. A process of bleaching cellulosic material and the like, comprising pre-bleaching said material with a gaseous bleaching agent, subjecting said material to a second stage of bleaching in a bath rendered alkaline with an alkali earth base, said second stage being conducted with a relatively low pulp concentration and a sufficiently high concentration of bleaching agent, so that a substantial excess thereof remains at the completion of said second stage, the conditions of the second stage being adjusted so as to preserve the fiber strength and avoid substantial dissolving action, and in the presence of calcium ions, and subjecting said material to a final bleaching stage under acid conditions for a relatively short period of time.

9. A process of bleaching cellulosic material and the like, comprising feeding said material in a comminuted, porous, moist condition into a reaction chamber, said material being fed into said reaction chamber through a conduit in such a manner that gas escaping from said chamber must pass through the cellulosic material in said conduit, forming a pile in said chamber with a free space thereabove, introducing a bleaching gas into said chamber above said pile and reacting on the material in said pile with said gas to substantial exhaustion of the gas, adding an aqueous diluent to the lower portion of said pile, said pile serving as a seal between the gas in the free space of said chamber and the aqueous diluent, and withdrawing said material from the lower diluted portion of said pile and through an aqueous seal of said chamber.

10. A process of bleaching cellulosic material and the like, comprising feeding said material in a comminuted, porous, moist condition into a reaction chamber, said material being fed into said reaction chamber through a conduit in such a manner that gas escaping from said chamber must pass through the cellulosic material in said conduit, forming a pile in said chamber with a free space thereabove, introducing a bleaching gas into the path of said material and allowing said gas to collect above said pile, and reacting on the material in said pile with said gas to substantial exhaustion of the gas, adding an aqueous diluent to the lower portion of said pile, said pile serving as a seal between the gas in the free space of said chamber and the aqueous diluent, and withdrawing said material from the lower diluted portion of said pile and through an aqueous seal of said chamber.

11. A process of bleaching cellulosic material and the like, comprising pre-bleaching said material to a relatively high degree in a so-called hypochlorite bath to which a sufficient amount

of acid has been added to render said bath distinctly acid, subjecting said material to a second stage of bleaching in a bath rendered alkaline with an alkali earth base and with the use of a relatively large excess of bleaching agent throughout the entire second stage, the conditions of the second stage being adjusted so as to preserve the fiber strength and avoid substantial dissolving action, and subjecting said material to a final bleaching stage under acid conditions for a relatively short period of time, said last two bleaching stages being conducted without any substantial amount of agitation.

12. A process of bleaching cellulosic material and the like, comprising pre-bleaching said material to a relatively high degree in a so-called hypochlorite bath to which a sufficient amount of acid has been added to render said bath distinctly acid, subjecting said material to a second stage of bleaching in a bath rendered alkaline with an alkali earth base and with the use of a relatively large excess of bleaching agent throughout the entire second stage, the conditions of the second stage being adjusted so as to preserve the fiber strength and avoid substantial dissolving action, and in the presence of calcium ions, and subjecting said material to a final bleaching stage under acid conditions for a relatively short period of time.

13. A process of bleaching cellulosic material and the like, comprising pre-bleaching said material to a relatively high degree in a so-called hypochlorite bath to which a sufficient amount of acid has been added to render said bath distinctly acid, subjecting said material to a second stage of bleaching in a bath rendered alkaline with an alkali earth base, said second stage being conducted with a relatively low pulp concentration and a sufficiently high concentration of bleaching agent so that a substantial excess thereof remains at the completion of said second stage, the conditions of the second stage being adjusted so as to preserve the fiber strength and avoid substantial dissolving action, and in the presence of calcium ions, and subjecting said material to a final bleaching stage under acid conditions for a relatively short period of time.

14. A process of bleaching cellulosic material or the like for use in paper manufacture, comprising pre-bleaching said material under acid conditions, subjecting said material to a second stage of bleaching under alkaline conditions with a relatively high concentration of bleach, said alkaline conditions and excess of bleach being maintained throughout the entire second stage, said second stage being conducted with substantially no agitation, and then subjecting said material to a bleaching operation under acid conditions and with a relatively low concentration of bleach.

15. A process as defined in claim 14, wherein said second stage is conducted in the presence of calcium ions.

16. A process of bleaching cellulosic material and the like, comprising pre-bleaching said material under acid conditions in a hypochlorite bath, washing and thickening the pulp, subjecting it to a second bleaching operation under alkaline conditions maintained throughout the stage and with a sufficiently high concentration of hypochlorite bleach so that an excess thereof remains at the end of the second stage, substantial agitation being avoided throughout the second stage, thickening the material and removing a large portion of the excess of bleach remaining at the end of the second stage, adding water to the thickened pulp so as to produce a low consistency and low bleach concentration, adding sufficient acid to render the mixture distinctly acid, allowing the mixture to react under said conditions with substantially no agitation until the bleaching is completed, and then neutralizing the bleaching agent and washing.

17. A process as defined in claim 16, wherein the second stage is conducted in the presence of calcium ions.

18. The process of bleaching cellulosic material and the like, comprising pre-bleaching said material in a moist, porous condition by means of a gaseous chlorine bleach, washing the pulp, subjecting it to a second bleaching operation under alkaline conditions maintained throughout the stage and with a sufficiently high concentration of hypochlorite bleach so that an excess thereof remains at the end of the second stage, substantial agitation being avoided throughout the second stage, thickening the material and removing a large portion of the excess of bleach remaining at the end of the second stage, adding water to the thickened pulp so as to produce a low consistency and low bleach concentration, adding sufficient acid to render the mixture distinctly acid, allowing the mixture to react under said conditions with substantially no agitation until the bleaching is completed, and then neutralizing the bleaching agent and washing.

19. A process of bleaching cellulosic material and the like, comprising pre-bleaching said material, subjecting said material to a second stage of bleaching under alkaline conditions and with the use of a relatively large excess of bleaching agent throughout the entire second stage, the conditions of the second stage being adjusted so as to preserve the fiber strength and avoid substantial dissolving action, and, after removing a large part of said excess of bleach from said material, diluting said material with water and subjecting it to a final bleaching stage under acid conditions and at a relatively low bleach concentration for a relatively short period of time, the bleaching agent in each stage comprising active chlorine.

20. A process of bleaching cellulosic material and the like, comprising pre-bleaching said material, subjecting said material to a second stage of bleaching in a bath rendered alkaline with an alkali earth base, said second stage being conducted with a relatively low pulp concentration and a sufficiently high concentration of bleaching agent so that a substantial excess thereof remains at the completion of said second stage, the conditions of the second stage being adjusted so as to preserve the fiber strength and avoid substantial dissolving action, and subjecting said material to a final bleaching stage under acid conditions for a relatively short period of time, the bleaching agent in each stage comprising active chlorine.

21. A process as defined in claim 8, wherein the bleaching agent comprises active chlorine in each stage.

22. A process as defined in claim 9, wherein the cellulosic material is fed into the top of the reaction chamber by means of a vertical conduit in which said material is allowed to collect in one or more piles, which piles of material act as seals for the absorption of bleaching gas and from which said material is dropped into said reaction chamber in finely divided form.

23. A process of bleaching cellulosic material and the like, comprising pre-bleaching said material with a gaseous bleaching agent, subjecting

said material to a second stage of bleaching under alkaline conditions with the use of a relatively large excess of bleach throughout the entire second stage, the conditions of the second stage being adjusted so as to preserve the fiber strength and avoid substantial dissolving action, and subjecting said material to a final bleaching stage under acid conditions for a relatively short period of time, the bleaching agent in each stage comprising chlorine.

24. A process as defined in claim 6, wherein the pulp in the first stage is dropped in a porous, moist condition through a space containing the gaseous bleaching agent.

25. A process as defined in claim 7, wherein the pulp in the first stage is dropped in a porous, moist condition through a space containing the gaseous bleaching agent.

26. A process as defined in claim 8, wherein the pulp in the first stage is dropped in a porous, moist condition through a space containing the gaseous bleaching agent.

27. A process of bleaching cellulosic material and the like, comprising pre-bleaching said material to a relatively high degree under acid conditions, subjecting said material to a second stage of bleaching under conditions maintained alkaline throughout said second stage with a large proportion of calcium ions, and with the use of a quantity of bleaching agent largely in excess of the quantity required in said second stage, said second stage being terminated before said material is completely bleached, and, after removing a large part of said excess of bleach from the material, subjecting the material to a final bleaching stage under acid conditions, at low consistency, and at a relatively low bleach concentration for a relatively short period of time, to attain a high white bleaching effect, the bleaching agent in each stage comprising chlorine.

28. A process of bleaching cellulosic material and the like, comprising pre-bleaching said material to a relatively high degree under acid conditions, subjecting said material to a second stage of bleaching under conditions maintained alkaline throughout said second stage with a large proportion of calcium ions, and with the use of a quantity of bleaching agent equal to a plurality of times the quantity required in said second stage, said second stage being terminated before said material is completely bleached, and, after removing a large part of said excess of bleach from the material, subjecting the material to a final beaching stage under acid conditions, at low consistency, and at a relatively low bleach concentration for a relatively short period of time, to attain a high white bleaching effect, the bleaching agent in each stage comprising chlorine.

29. A process of bleaching cellulosic material and the like, comprising pre-bleaching said material to a relatively high degree under acid conditions, subjecting said material at a low consistency and in the absence of substantial agitation to a second stage of bleaching under conditions maintained alkaline throughout said second stage with a large proportion of calcium ions, and with the use of a quantity of bleaching agent largely in excess of the quantity required in said second stage, said second stage being terminated before said material is completely bleached, and, after removing a large part of said excess of bleach from the material, subjecting the material to a final bleaching stage under acid conditions, at low consistency, and at a relatively low bleach concentration for a relatively short period of time, to attain a high white bleaching effect, the bleaching agent in each stage comprising chlorine.

30. A process of bleaching cellulosic material and the like, comprising pre-bleaching said material to a relatively high degree under acid conditions, subjecting said material at a low consistency and in the absence of substantial agitation to a second stage of bleaching under conditions maintained alkaline throughout said second stage with a large proportion of calcium ions, and with the use of a quantity of bleaching agent equal to a plurality of times the quantity required in said second stage, said second stage being terminated before said material is completely bleached, and, after removing a large part of said excess of bleach from the material, subjecting the material to a final bleaching stage under acid conditions, at low consistency, and at a relatively low bleach concentration for a relatively short period of time, to attain a high white bleaching effect, the bleaching agent in each stage comprising chlorine.

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